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MANUFACTURE OF AROMATIC CARBONATE ESTERS

Inventors:

Hiroshi Iwane
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Takahiro Komeyama
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Masatoshi Takaki
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Hidekazu Miyagi
Mitsubishi Chemical Corp.
Tsuba Research Laboratory
8-3-1 Chuo-ku, Ami-machi,
Inashiki-gun, Ibaraki-ken

Applicant:

000005968
Mitsubishi Chemical Corp.
2-5-2 Marunouchi,
Chiyoda-ku, Tokyo

Agent:

Takachi Yamamoto,
patent attorney

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Abstract

Constitution

A method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, where said reaction is carried out in a reaction system in the presence of, (A) one or more substances selected from palladium or palladium compounds, (B) one or more substances selected from manganese compounds, and (C) one or more substances selected from inorganic halides such as alkali metal halides and alkaline earth metal halides.

Effect

A method for efficiently manufacturing aromatic carbonate esters is offered that solves problems with catalyst systems that have been offered in the past related to cases where reactions progress at a sufficiently high initial rate, but stop midway, or where hydrolysis of the aromatic carbonate ester occurs due to by-product water when a manganese compound is used as an auxiliary catalyst, and cases where the reaction rate is generally slow when a cobalt compound is used as an auxiliary catalyst.

Claims

1. A method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing

aromatic carbonate esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) one or more manganese salts, and (C) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides.

2. The method according to Claim 1, wherein the inorganic halide is a substance selected from chloride and bromide.

3. The method according to Claim 2, wherein the chloride is cesium chloride.

4. The method according to Claim 2, wherein the bromide is a substance selected from sodium bromide, potassium bromide, rubidium bromide, cesium bromide and barium bromide.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns a method for the manufacture of aromatic carbonate esters using special catalysts. Aromatic carbonate esters, particularly diphenyl carbonate, are useful as raw materials in the production of polycarbonate and other substances.

[0002]

Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene are allowed to react have been used as methods for manufacturing aromatic carbonate esters. However, these methods encounter numerous problems in terms of a method for industrial manufacture due to the high toxicity of phosgene and due to the fact that large quantities of by-product inorganic salt are produced. Thus, a number of methods have been offered that do not use phosgene whereby aromatic carbonate esters are manufactured in a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen.

[0003]

With regard to catalysts that are used in such methods, a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38144 wherein a palladium compound, a compound containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38145 wherein a palladium compound, manganese complex, cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551 wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564 wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and

quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754 wherein a palladium compound, cobalt compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095, wherein a palladium or palladium compound, cobalt compound, halide and basic compound are used; a method is offered in Japanese Kokai Patent Application No. Hei 5[1993]-97775 (U.S. Patent No. 5,142,086), wherein a catalyst comprising a palladium compound, quaternary ammonium salt, metal auxiliary catalyst selected from cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chromium and copper, and organic auxiliary catalyst selected from an aromatic ketone, aliphatic ketone or aromatic polycyclic hydrocarbon is used; and a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-58961, wherein palladium or a palladium compound, cobalt compound, and alkali metal halide are used.

[0004]

However, these methods are not satisfactory for use as methods for industrial manufacture due to problems with insufficient catalytic activity and low yield of aromatic carbonate ester with respect to the aromatic hydroxy compound. Based on the supposition that water generated in the reaction decreases catalytic activity, and also promotes hydrolysis of the aromatic carbonate ester with conventional catalyst systems, a method whereby a large quantity of desiccant is added in order to eliminate the water that is generated (Japanese Kokai Patent Application No. Sho 54[1979]-135744), a method whereby the water is distilled off by distillation of the reaction products

(Japanese Kokai Patent Application No. Hei 4[1992]-261142) and other preventative methods have been offered. However, the effects of these methods have been inadequate.

[0005]

Problems to be solved by the invention

The inventors of the present invention et al., based on the results of investigations into addition formats and other conventional technology wherein phenol is used as a substrate, discovered that when a manganese compound is used as catalyst, the initial reaction progresses at a satisfactory rate, but slows as hydrolysis of the aromatic carbonate ester proceeds due to water that is generated. It was also discovered that reaction rates are slow in general when cobalt compounds are used as auxiliary catalysts. The present invention solves these problems of catalyst systems that have been proposed in the past, and offers a method for the efficient manufacture of aromatic carbonate esters.

[0006]

Means to solve the problems

Specifically, the present invention is a method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonate esters being characterized in that said reaction is carried out in a

reaction system in the presence of (A) one or more substances selected from palladium and palladium compounds, (B) one or more manganese salts, and (C) one or more inorganic halides selected from alkali metal halides and alkaline earth metal halides.

[0007]

1. Reaction raw materials

1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention is an aromatic mono- or polyhydroxy compound. Examples include phenol; p-cresol, 2,6-xyleneol, 2,4,6-trimethylphenol, 2,3,4,5-tetramethylphenol, ethylphenol, propylphenol methoxyphenol, ethoxyphenol, chlorophenol, 2,4-dichlorophenol, bromophenol, 2,4-dibromophenol and other substituted phenols and isomers thereof; naphthol, 2-methylnaphthol, 2-ethylnaphthol, 2-chloronaphthol, 2-bromonaphthol and other substituted naphthols and isomers thereof; 2,2-bis(4-hydroxyphenyl)propane and various other bisphenols and stereoisomers thereof; 4,4'-biphenol and various other biphenols and stereoisomers thereof; 4-hydroxypyridine and various other heteroaromatic hydroxy compounds and stereoisomers thereof; as well as compounds thereof produced by substitution with alkyl groups or halogen atoms. Of these compounds, phenol is particularly desirable.

[0008]

(2) Carbon monoxide

The carbon monoxide that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as nitrogen, argon, carbon dioxide or hydrogen.

[0009]

(3) Oxygen

The oxygen that is used in the present invention can be a gas that is produced by starting with a high-purity substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as air, nitrogen, argon, carbon dioxide or hydrogen.

[0010]

2. Catalyst

(A) Palladium and palladium compounds

The palladium and palladium compounds that are used in the present invention are palladium black; palladium/carbon, palladium/alumina, palladium/silica or other palladium/porous carriers systems; palladium chloride, palladium bromide,

palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate or other organic palladium acid salts. In addition, substances that can also be used include palladium (II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins with palladium, examples of which include $\text{PdCl}_2(\text{PhCN})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, and $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, or mixtures of palladium with compounds generated by these complexes in the reaction system. The amount of palladium component that is used in the reaction has no particular restrictions, but a mole ratio in the range of 1 to 10^{-5} with respect to the aromatic hydroxy compound is desirable, with a range of 10^{-1} to 10^{-4} being particularly desirable.

[0011]

(B) Manganese salt

The manganese salt that is used in the present invention is preferably a divalent or trivalent manganese salt, examples of which include manganese (II) fluoride, manganese (II) chloride, manganese (II) bromide, manganese (II) iodide, manganese (II) sulfate, manganese (II) carbonate, manganese (II) nitrate and other inorganic salts; manganese (II) formate, manganese (II) or (III) acetate, manganese (II) butyrate and other organic acid salts; manganese (II) or (III) acetylacetonate, complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on these salts; and mixtures of manganese salts and compounds formed in the reaction system by

these complexes. There are no particular restrictions on the amount of manganese component that is used in the reaction, but a molar ratio in the range of 10^{-3} to 10^2 with respect to the palladium component (A) is preferred, with a range of 10^{-2} to 10 being particularly desirable.

[0012]

(C) Inorganic halide

The halide that is used in the present invention is an alkali metal or alkaline earth metal halide. Examples of preferable halides include chlorides and bromides, with cesium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide and barium bromide being preferred. There are no particular restrictions on the amount of inorganic halide that is used in the present invention, but a mole ratio in the range of 10^{-2} to 10^3 with respect to the palladium component (A) is preferred, with a range of 10^{-1} to 10^2 being particularly desirable. In addition, it is preferable for the mole ratio to be in the range of 10^{-4} to 1 with respect to the aromatic hydroxy compound, with a range of 10^{-3} to 10^{-1} being particularly desirable.

[0013]

3. Reaction method and conditions

The reaction is performed by introducing the aforementioned aromatic hydroxy compound and the aforementioned components

(A)-(C) into the reactor, pressurizing the system with carbon monoxide and oxygen, and then carrying out the reaction while stirring well and heating. The reaction pressure is 1-500 atm total pressure, with a range of 1-250 atm being preferred. The oxygen partial pressure is 0.1-6 atm, with a range of 0.5-2 atm being preferred. If the oxygen partial pressure is too high, reaction between the aromatic hydroxy compound and halogen will occur in conjunction, which is undesirable.

[0014]

The compositional ratio of carbon monoxide and oxygen can be set at a freely determined ratio, but from the standpoint of safety, it is preferable for a compositional ratio to be used that is outside the combustion range. Moreover, it is also effective to dilute the substances with inert gas that does not have a detrimental influence on the reaction. It is undesirable for the amount of diluent gas to be too great, as this causes the carbon monoxide and oxygen partial pressures to decrease. The reaction gas composition cannot be monolithically defined, as the combustion range changes depending on the temperature, pressure and diluent gas, but ordinarily, carbon monoxide is used in excess, with the oxygen at 1-10% with respect to the total pressure, and the diluent gas at about 0-50% with respect to the total pressure. In addition, when one of the gas components is depleted as the reaction progresses, pressure can be supplied at certain times, or a mixed gas of uniform composition can be supplied continuously under pressure to the reactor. The reaction temperature is in the range of 70-150°C. The reaction time varies

depending on the reaction conditions, but is ordinarily a few minutes to a few hours.

[0015]

Examples of solvent that can be used in the reaction include hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane ethyl acetate, methyl formate, acetonitrile and other inert solvents. There are cases where the raw material aromatic hydroxy compound serves as the reaction solvent, and it is not particularly necessary to use another solvent in such cases. After completion of the reaction, the reaction mixture is subjected to filtration as is in order to separate the solids. High-purity aromatic carbonate can then be purified and isolated by means of a purification method such as fractionation purification or crystallization. Moreover, the catalyst component that is obtained as filtrant or as distillation residue can then be recovered and used again in subsequent reactions without modification.

[0016]

Application examples

The present invention is described in detail below by providing application examples and comparative examples.

Application Example 1

1.88 g (20 mmol) of phenol, 21.4 mg (10 μ g atom Pd) of 5% palladium/carbon, 2.5 mg (10 μ mol) of manganese (II) acetate tetrahydrate and 35.7 mg (0.30 mmol) of potassium bromide were introduced into a Hastelloy autoclave with an inner volume of 40 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 60 atm, dry air was introduced at 5 atm (oxygen partial pressure 1 atm), and the reactants were mixed by stirring for 3 h at 120°C using a stir bar. After completion of the reaction, the gas phase and liquid phase were each subjected to analysis by gas chromatography. The results indicated a diphenyl carbonate yield of 3.92% (0.40 mmol) with respect to the phenol. Carbon dioxide was a by-product at 0.55 mol, but by-products of o- and p-bromophenol were not seen.

[0017]

Comparative Example 1

A reaction was carried out in the same manner as in Application Example 1, with the exception that potassium bromide was not used. The results indicated that although by-products of o- and p-bromophenol were not seen, the yield of diphenyl carbonate was [only] 0.2%.

[0018]

Comparative Example 2

A reaction was carried out in the same manner as in Application Example 1, with the exception that 2.5 mg (10 μ mol) of cobalt (II) acetate tetrahydrate was used instead of 2.5 mg of manganese (II) acetate tetrahydrate. The results indicated that although by-products of o- and p-bromophenol were not seen, the diphenyl carbonate yield was [only] 1.01%.

[0019]

Application Examples 2-6

A reaction was carried out in the same manner as in Application Example 1, with the exception that the various manganese salts shown in Table I were used instead of manganese (II) acetate tetrahydrate. The yield of diphenyl carbonate with respect to phenol and the amount of by-product carbon dioxide are shown in Table I. In each case, by-products of o- and p-bromophenol were not seen.

[0020]

Table I
//insert from p.4//

Key: 1	Application Example
2	Manganese salt
3	Diphenyl carbonate yield
4	Carbon dioxide
5	Manganese (III) acetate dihydrate
	Manganese (II) benzoate tetrahydrate
	Manganese (III) acetylacetonate
	Manganese (II)acetylacetonate dihydrate
	Manganese (II) fluoride

[0021]

Application Examples 7-11

A reaction was carried out in the same manner as in Application Example 1, with the exception that the various inorganic halides shown in Table II were used. The yield of diphenyl carbonate with respect to phenol and the amount of

by-product carbon dioxide are shown in Table II. In each example, no by-products of o- and p-bromophenol were seen.

[0022]

Table II

//insert from p.4//

Key: 1 Application Example
 2 Inorganic halide
 3 Diphenyl carbonate yield
 4 Carbon dioxide

[0023]

Application Example 12

A reaction was carried out in the same manner as in Application Example 1, with the exception that the reaction temperature was changed to 100°C. The results indicated a diphenyl carbonate yield of 2.33%, and although carbon dioxide by-product was 0.17 mmol, no by-products of o- or p-bromophenol were seen.

[0024]

Application Example 13

A reaction was carried out in the same manner as in Application Example 1, with the exception that 2.2 mg (10 μ g atom Pd) of palladium (II) acetate was used instead of 21.4 mg of 5% palladium/carbon. The results indicated a diphenyl carbonate yield of 2.41%. Although carbon dioxide by-product was 0.67 mmol, no by-products of o- or p-bromophenol were seen.

[0025]

Application Example 14

A reaction was carried out in the same manner as in Application Example 1, with the exception that carbon monoxide was introduced at 30 atm rather than at 60 atm. The results indicated a diphenyl carbonate yield of 2.22%. Although carbon dioxide by-product was 0.36 mmol, no by-products of o- or p-bromophenol were seen.

[0026]

Application Example 15

A reaction was carried out in the same manner as in Application Example 1, with the exception that, after initiation of the reaction, a procedure was repeated wherein gas was extracted every hour, and after replacing the interior of the

system with carbon monoxide, carbon monoxide was introduced at 60 atm and dry air was introduced at 5 atm. The results indicated a diphenyl carbonate yield of 6.10%. Although carbon dioxide by-product was 1.28 mmol, no by-products of o- or p-bromophenol were seen.

Japanese Kokai Patent Application No. Hei 7[1995]-145107

Translated from Japanese by the Ralph McElroy Co., Custom Division
P.O. Box 4828, Austin, Texas 78765 USA